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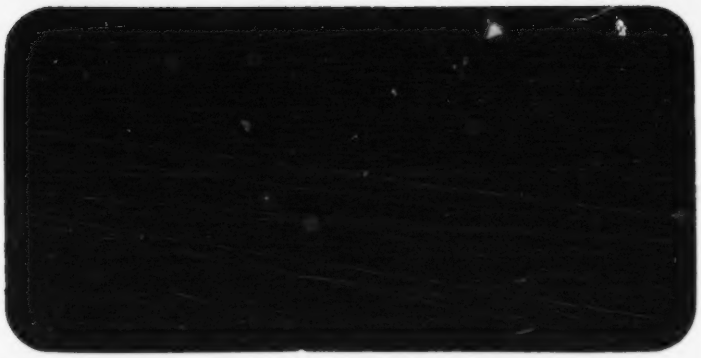

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Overcoming the brightness ceiling for mechanical pulps prepared from blue-stained lodgepole pine chips

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Abstract

The initial brightness of thermomechanical pulps (TMPs) and chemithermomechanical pulps (CTMPs) prepared from chip blends containing mountain pine beetle-infested (kill date = 2-3 years), blue-stained lodgepole pine (LPP) is up to 5.0 ISO points lower than that of the pulps made from the green LPP chips; the higher the blue-stained chip content in the chip blends, the lower the initial brightness of the pulps. Paprican's VIS-NIR technique has been shown to be capable of predicting the blue-stained chip content in the chip blends accurately on a pilot-plant conveyor.

Thermomechanical pulps made from chip blends with various blue-stained chip contents all have lower sodium hydrosulfite (Y) bleaching response than TMP pulp made from the green chips; the brightness of the Y-bleached, blue-stained TMP is up to 7.8 ISO points lower than the Y-bleached, green TMP. A method to overcome the brightness ceiling of Y-bleached TMP made from chip blends with 25% blue-stained chip content has been developed. The method involves the addition of 0.2% (o.d. pulp) of sodium borohydride to Y bleaching of the pulp.

A high bleaching end pH in alkaline hydrogen peroxide (P) bleaching has been discovered to be capable of removing most or all of the blue stain in TMP pulps made from chip blends with 50-100% blue-stained chip contents. Thus, optimal P bleaching conditions (for example, $H_2O_2 \geq 5.0\%$ o.d. pulp, end pH = ~10.0) have been identified to allow the bleaching of the TMP made from chip blends with 50% blue-stained chip content to the same brightness as the bleaching of the pulp from the green chips. However, the brightness of the TMP made from 100% blue-stained chips and bleached with P under optimal bleaching conditions is still 0.8 ISO points lower than that of the P-bleached, green TMP.

Chemithermomechanical made from the 100% blue-stained chips can be bleached with alkaline hydrogen peroxide (P) to the same brightness as CTMP made from the green chips, due to the complete removal of the blue stain during P bleaching.

The blue stain in the sapwood of mountain pine beetle-infested LPP appears to be the fungal melanin pigments. The blue stain chips have a lower triglyceride content than the green chips. The DMSO-soluble, lignin-carbohydrate-complex-poor fraction from the blue-stained chips appears to contain the blue stain, as only this fraction shows significant chemical difference from that of the green chips; its SEC chromatogram contains slightly more low-molecular weight UV-absorbing material.

Keywords: Bleaching, Blue stain, Brightness, Chelation, Chemithermomechanical pulps, Fungi, Hydrogen peroxide, Mechanical pulps, Mountain pine beetle, Pigment, Sodium borohydride, Sodium hydrosulfite, Thermomechanical pulps

Résumé

La brillance initiale des pâtes thermomécaniques (TMP) et chimico-thermomécaniques (CTMP) préparées à partir de mélanges de copeaux contenant du pin tordu bleuis infestés par le dendroctone du pin (date de mort = 2 ou 3 ans) peut être inférieure de 5,0 points ISO à celle des pâtes préparées avec des copeaux de pin tordu verts. Plus la quantité de pin bleui est élevée dans les mélanges de copeaux, moins les pâtes obtenues sont brillantes. On a démontré que la technique VIS-NIR de Paprican permet de prédire avec précision la quantité de copeaux bleuis dans les mélanges de copeaux sur le convoyeur d'une usine-pilote.

Les pâtes thermomécaniques faites à partir de mélanges de copeaux contenant des copeaux bleuis ont une réaction de blanchiment au dithionite de sodium (Y) inférieure aux pâtes TMP faites à partir de copeaux verts. La brillance des pâtes TMP bleuies blanchies au Y peut être inférieure de 7,8 points ISO à celle des pâtes TMP vertes blanchies au Y. Une méthode pour dépasser la limite de brillance des pâtes TMP blanchies au Y et contenant 25 % de copeaux bleuis a été mise au point. La méthode comprend l'ajout de 0,2 % (pâtes séchées au four) de borohydrure de sodium au blanchiment Y de la pâte.

On a découvert qu'un pH final de blanchiment élevé en peroxyde d'hydrogène alcalin (P) permet d'éliminer en partie ou en totalité le bleuissement des pâtes TMP préparées avec des mélanges de copeaux contenant 50 à 100 % de copeaux bleuis. Ainsi, des conditions optimales de blanchiment P (par exemple, $H_2O_2 \geq 5,0$ % pâte séchée au four, pH final = ~10,0) ont été déterminées afin d'obtenir une même brillance pour les pâtes TMP faites à partir de mélanges de copeaux contenant 50 % de copeaux bleuis que pour les pâtes TMP composées de copeaux verts. La brillance des pâtes TMP faites uniquement à partir de copeaux bleuis et blanchies au P dans des conditions de blanchiment optimales est toutefois inférieure de 0,8 point ISO à celle des pâtes TMP vertes blanchies au P.

Il est possible d'obtenir la même brillance avec les pâtes chimico-thermomécaniques faites uniquement à partir de copeaux bleuis blanchies avec du peroxyde d'hydrogène alcalin (P) qu'avec les pâtes CTMP faites à partir de copeaux verts en raison de l'élimination complète du bleuissement pendant le blanchiment au P.

Le bleuissement de l'aubier des pins tordus infestés par le dendroctone du pin semble être attribuable à des pigments de mélanine fongique. Les copeaux bleuis ont une teneur en triglycérides inférieure à celle des copeaux verts. La fraction faible en complexe lignine-carbohydrate soluble au DMSO des copeaux bleuis semble contenir le bleuissement, puisque seule cette fraction présente des différences chimiques importantes par rapport à celle des copeaux verts. Sa chromatographie par perméation sur gel contient un peu plus de matières à faible masse moléculaire absorbant les UV.

Mots-clés : Blanchiment, bleuissement, brillance, chélation, pâtes chimico-thermomécaniques, champignons, peroxyde d'hydrogène, pâtes mécaniques, dendroctone du pin ponderosa, pigment, borohydrure de sodium, dithionite de sodium, pâtes thermomécaniques.

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1 Introduction

1.1 Rational of the Project

Intrinsic strength and brightness of spruce, pine and fir (SPF) wood chips used to prepare value-added high-brightness mechanical pulp grades sets SPF mechanical pulps apart on the world stage. BC's mechanical pulping and papermaking operations lead the world in the development of novel grades of paper based upon the unique attributes of SPF. Prior research funded in part by the Canadian Forest Service Mountain Pine Beetle Initiative clearly demonstrated a poor hydrosulfite brightening response of mechanical pulps prepared from blue-stained lodgepole pine chips [Hu et al. 2006]. In addition, a brightness ceiling was observed. The blue-stained thermomechanical pulps, when treated with low doses of hydrogen peroxide (1-3%), also exhibited poor brightening response relative to the control. Processing a large percentage of blue-stained lodgepole pine chips within the SPF chip supply has the potential to place BC's mechanical pulping operations at a significant cost and quality disadvantage against its competitors. This project seeks to determine the fundamental causes of the brightness ceiling, to develop practical laboratory-tested means to overcome this challenge, and to bring together a blue stain quantification tool/sensor and the technical (economic) effects of mechanically pulping much higher levels of blue stain-affected SPF chips.

1.2 Blue Stain Chemistry

Although the formation of blue stain in the sapwood of lodgepole pine (LPP) trees infested by the mountain pine beetle has been known for decades, the chemical compositions of the blue stain remain speculative. Fungal metabolites such as 2,3-dihydroxybenzoic acid have been isolated from four *Ceratocystis* species of blue-staining fungi in artificial media and shown to form intensely blue complexes with ferric ions (Fe^{3+}); such blue complexes were proposed to be a key contributor of the blue stain [Ayer et al. 1986]. However, efforts to extract such blue complexes from, and prove their contribution to the blue colouration of the sapwood of beetle-killed LPP trees were unsuccessful [Ayer and Migaj 1988].

The fungal pigments of melanin types responsible for the dark colouring of the hyphae of two species of blue-staining fungi (*Ceratocystis coerulescens* and *Alternaria alternata*) have been isolated from culture medium and proposed to be responsible for the blue stain [Zink and Fengel 1988]. Melanins are biopolymers of phenolic compounds that may contain nitrogen or sulfur and have black, brown or yellow-red color depending on their biosynthesis [Plonka and Grabacka 2006]. They are characterized by their insolubility, resistance to hydrolysis, lack of molecular regularity and poorly defined structures. They are, however, known to be soluble in alkali and can be discoloured by reaction with H_2O_2 [Nicolaus 1968].

1.3 Bleaching/Brightening of Mechanical Pulps

Industrial bleaching of mechanical pulps is currently achieved mainly by the use of alkaline hydrogen peroxide [Presley and Hill 1996] and/or sodium hydrosulfite (i.e.,

sodium dithionite) [Ellis 1996]. Alkaline hydrogen peroxide, in the presence of peroxide stabilizers such as sodium silicate and magnesium sulfate, is capable of providing a brightness gain of up to ~25 ISO points to most mechanical pulps. However, alkaline peroxide reduces the pulp yield by 2-5%, and produces effluent with high chemical oxygen demand [Brauer et al. 2001] due to oxidative degradation of lignin and hemicelluloses from the fibres. Sodium hydrosulfite is a cheap and selective brightening agent currently used by 45 mills in Canada and in the US to bleach ~12 million metric tons of mechanical pulps/year. However, sodium hydrosulfite can only provide a maximum brightness gain of ~10 ISO points to most mechanical pulps.

Several other reducing agents capable of bleaching mechanical pulps have been reported since the late 1950s. Such bleaching has been achieved with, for example, sodium borohydride, $NaBH_4$ [Mayer and Donofrio 1958]; formamidine sulfinic acid (FAS) [Blechschmidt et al. 1991]; $(H_2N)_2CSO_3$ [Mayer and Donofrio 1958]; and sodium bisulfite, $NaHSO_3$ [Kuys and Abbot 1996]. None of these agents have been used commercially for the bleaching of virgin mechanical pulps because of their high cost, high toxicity or low bleaching ability. Applications for FAS has been found in the bleaching and/or color stripping of recycled fibres including mixed office waste [Kronis 1996; Fillion et al. 2006].

A recent Paprican/University of British Columbia collaboration has led to the discovery of a new class of promising, phosphorus-based bleaching agents for mechanical pulps and the development of proprietary technologies using these agents [Hu and James 2004; Hu et al. 2004]. One of these agents, tetrakis(hydroxymethyl)phosphonium sulfate (THPS), $[P(CH_2OH)_4]_2SO_4$, has been successfully tested on a commercial scale and used as a complementary bleaching agent to sodium hydrosulfite in the commercial bleaching of a spruce stone-ground wood (SGW) pulp to higher brightness [Hu et al. 2007]. Use of THPS as a complementary bleaching agent to sodium hydrosulfite may enable the bleaching of mechanical pulps prepared from blue-stained chips to higher brightness. The reducing agents, $NaBH_4$ and FAS, may also be able to complement sodium hydrosulfite in the bleaching of mechanical pulps prepared from blue-stained chips.

1.4 Objective of the Project

The objective of the project is to develop a novel, cost effective approach to brightening mechanical pulps prepared from blue-stained lodgepole pine chips to maintain current markets and assist with SPF-based wood-containing grade development.

1.5 Approaches of the Project

The approaches of the project are: 1) to prepare in the pilot-plant a series of five thermomechanical pulps (TMPs) and five chemithermomechanical pulps (CTMPs) containing increasing proportions of blue stain from green and extremely blue-stained LPP chips and their blends, and to test and quantify the blue stain contents of the chip blends and the pulps using Paprican's Vis-NIR spectrometer; 2) to evaluate the effectiveness of pretreatment of the blue-stained TMP pulps with a small amount of

caustic, sodium bisulfite or the novel bleaching agent, THPS, and to evaluate the effectiveness of using reductive bleaching chemicals, $NaBH_4$, FAS, and THPS as complementary bleaching agents to sodium hydrosulfite, in overcoming the brightness ceiling of sodium hydrosulfite bleaching of these pulps; and 3) to perform alkaline peroxide bleaching of the blue-stained TMP and CTMP pulps to high brightness, study the bleach effluent quality, and determine the fundamentals of blue stain and causes for the poor hydrosulfite brightening response of blue-stained TMP pulps.

2 Material and Methods

2.1 Chip Samples and Characterization

Six lodgepole pine (LPP) trees (*Pinus contorta* var. *latifolia*) (Pli) were harvested from one site in the MSxk biogeoclimatic subzone near Kamloops, BC in November 2005. Three of these stems were healthy live Pli (green) and three were mountain pine beetle "red attack" ones. Mountain pine beetle-induced death on the three red-attacked trees was confirmed by the presence of pitch tubes on the bark, blue stain fungi in the sapwood, and red foliage. The estimated kill date of these three trees was summer 2003. Thus, the time-since-death (TSD) for the red-attacked, blue-stained LPP trees was 2-3 years. Disks of the three green and the three blue-stained LPP trees were collected from approximately one meter intervals starting at breast height (1.3 m) to a maximum of 6.3 meters.

The green and the blue-stained LPP disks were shipped to Paprican's Vancouver laboratory, and their mature (over 40 years) sapwood sections were obtained using a portable sawmill. The mature sapwood sections of the green and the blue-stained samples were chipped, respectively, using a CM&E 10-knife disc chipper. Each of the three chip samples was screened on a Burnaby Machinery and Mill Equipment Ltd. two-deck laboratory chip classifier to remove oversize (>31 mm) and fine (<8 mm) material before their moisture content (MC) (wet basis) was determined (Table 1). Chip packing and basic densities were determined by a literature method [Hatton 1979] and according to a modified PAPTAC Standard Method A.8P, respectively (Table 1).

Table 1. Characteristics of the green and blue-stained LPP chips.

Chips	Packing Density (kg/m^3)	Basic Density (kg/m^3)	Moisture Content (%) (wet basis)
Green	173	381	56.4
Blue-stained	188	408	20.8

Samples of the green (referred to as healthy) and the blue-stained (referred to as infected) chips were fractionated by successive extractions with acetone, dioxane (after ball milling) and dimethylsulfoxide (DMSO) and characterized (with or without acetylation) by Fourier-transform Infrared (FTIR), elemental, Klason lignin and sugar analyses, and by proton (^1H), carbon-13 (^{13}C) and two-dimensional Heteronuclear Single-Quantum Correlation (HSQC) Nuclear Magnetic Resonance (NMR) spectroscopy, size exclusion chromatography (SEC) and gas chromatography/electron ionization mass spectrometry

(GCMS) at the University of British Columbia Department of Wood Science by Drs John Kadla and Jennifer Braun.

The blue-stained and the green LPP chips were combined in three different blends with blue-stained chip contents of 25, 50 and 75%. The blue-stained chip content (%) is defined as [weight of blue-stained chips/(weight of blue-stained chips + weight of green chips)] x 100; all weights are on oven-dried (o.d.) basis. Throughout this report, 0, 25, 50, 75 and 100% blue-stained (C)TMP refer to (C)TMP prepared from chips (or chip blends) with 0, 25, 50, 75 and 100% blue-stained chip contents, respectively.

2.2 Quantification of Blue-stained Chip Content by VIS-NIR Technique

Chip blends with many known blue-stained chip contents were also prepared and analyzed for blue-stained chip contents on a laboratory rotating tray with a measured area of ~300 cm^2 using Paprican's Vis-NIR spectrometer.

Additional chip blends were also prepared and measured on-line on a pilot-plant conveyor system, which is smaller but similar to a mill conveyor. These chip blends were dried to the same moisture content of 10.0 ± 0.5%, and 16 blends were measured. Eight blends were used to generate a predictive model, while eight blends were used to test the predictive ability of the model. The model was based on the spectral region of 400-1100 nm. For the 16 measured blends, in total 633 spectra were measured (414 on training set blends and 219 on test set blends). In calculating the model, all spectra for the training set blends were used (414 spectra). In predicting the test set blends, all spectra were used for prediction (219 spectra) and the average prediction for each blend was calculated.

2.3 Pilot-plant Mechanical Pulping

The green chips, the three chip blends and the blue-stained chips with blue-stained chip contents of 0, 25, 50, 75 and 100% were used to prepare 0, 25, 50, 75 and 100% blue-stained TMP (or CTMP), respectively. For the preparation of the TMP pulps, the chips (or chip blends) were first subjected to first-stage refining in a 30.5-cm Sunds Defibrator TMP 300 single-disc laboratory refiner which was connected to a Labview PC system to allow the control and monitoring of the refining variables. For the preparation of the CTMP pulps, 3.8-4.4% (o.d. wood) of sodium sulfite, Na_2SO_3, was applied to the chips (as 3.5% Na_2SO_3 solution at pH 10.1) at the built-in screw impregnator in the refiner. For the preparation of both TMP and CTMP pulps, various amounts of dilution H_2O were added to the refiner to give a constant, discharge pulp consistency of 23-29%. Pertinent refining conditions for the first-stage TMP and CTMP pulping are given in Table 2.

The first-stage refined pulps were given two (for TMP pulps) or four (for CTMP pulps) further passes through a 30.5-cm Sprout Waldron open-discharge laboratory refiner equipped with type D2A507 plates to give TMP and CTMP pulps (~2.5 kg o.d. each) with Canadian Standard Freeness (CSF) values of ~100 mL.

Table 2. First-stage refining conditions using 30.5-cm Sunds Defibrator TMP 300 single-disc laboratory refiner.

Plates	**rotor, No. 3809 modified; Stator, No. 3804 modified**
Preheater pressure	**152 kPa**
Refiner housing pressure	**179 kPa (~26 psi)**
Presteaming time	**10 min (atmospheric pressure)**
Residence time	**10 min**
Pulp consistency	**23 to 29% OD pulp (cyclone exit)**
Prex compression ratio	**3:1**

2.4 Bleaching of TMP or CTMP Pulps

2.4.1 Titration of pulp at 5% consistency (Cs) with 0.1 N NaOH

A sample (12 g o.d.) of each of the 0, 25, 50, 75 and 100% blue-stained TMP (or CTMP) pulps was diluted with deionized (DI) H_2O to give a 5.0% Cs. The pulp slurry (pH typically ~5.5) was titrated with 0.1 N NaOH and the amount required to reach any known pH (5.7-10.0) was recorded.

2.4.2 Sodium hydrosulfite (Y) bleaching/brightening

A known amount of DI H_2O needed to give a 5.0% Cs for the bleaching of 12 g (o.d.) of 0, 25, 50, 75 or 100% blue-stained TMP pulp was weighed out. Of the water, 50 mL was reserved and stored in plastic bottle in a refrigerator. The remaining water was added to the pulp (12 g o.d.) in a polyethylene bag, and the bag was sealed and placed in a water-bath heated to 70°C for 10 minutes. To the reserved water, a known amount of 0.1 N NaOH was added to give a desired "pulp initial pH" (pH 5.7-10.0) (i.e., the pH of the pulp at the start of bleaching if no bleaching chemicals were added) based on the results from the titration of the pulp described in section 2.4.1. A commercial, powder sodium hydrosulfite (Y) (0.6-1.2% o.d. pulp) was then added. The reserved water with added NaOH and Y was added to the preheated pulp. The bag was quickly sealed with air excluded from the headspace of the bag. The pulp inside the sealed bag was homogenized by hand mixing of the pulp from the outside of the bag. The sealed bag was then placed in a water-bath heated to 70°C for 1 hour. At the end of bleaching, the polyethylene bag was cooled in a cold water-bath to room temperature (~20°C). The pulp was diluted with DI H_2O to 1.0% Cs. The pH (end pH) of the pulp slurry was recorded, and adjusted to 6.0 with 0.1 N H_2SO_4 if the end pH was > 6.0. The pulp slurry was filtered with the filtrate being recycled once to recover the fines. The same dilution, pH adjustment (if needed) and filtration were then repeated once. The filtered pulp was used to make three handsheets (200 g/m^2) according to PAPTAC Test Methods, Standard C.5. The %ISO brightness and CIE b* of the sheets were determined on a Technibrite Micro TB-1C instrument according to PAPTAC Test Methods, Standard E.1, and their average values were recorded.

2.4.3 *Pretreatment of 100% blue-stained TMP with caustic, sodium sulfite at various pHs, or pretreatment of 50% blue-stained TMP with DTPA, "DTPA + sodium hydrosulfite", "DTPA + $NaBH_4$", or "DTPA + FAS"*

A known amount of DI H_2O needed to give a 1.5% Cs for the pretreatment of 24 g (o.d.) of the blue-stained TMP pulp was weighed out and 30 mL of the water was reserved and stored in plastic bottle in a fridge. The remaining water was added to the pulp in a polyethylene bag, and the bag was sealed and placed in a water-bath heated to 50°C for 15 minutes. The pulp was transferred to a 2L-beaker and mixed.

For the caustic pretreatment, the reserved water was added to the pulp and the pH was adjusted to 9.0 with 0.1 N NaOH. For the sodium sulfite or DTPA pretreatment, the reserved water and 2.0% (o.d. pulp) of sodium sulfite or 0.5% (o.d. pulp) of diethylenetriaminepentaaetic acid (DTPA) in the form of its pentasodium salt, were added to the pulp, and the pH of the pulp slurry was adjusted to the desired value (pH 5.0-10.0). For the "DTPA + reducing agent" pretreatments, 0.5% (o.d. pulp) of DTPA was added to the pulp and the pH of the pulp slurry adjusted to a desired value (6.0 or 8.0). Sodium hydrosulfite, $NaBH_4$ (Fisher Canada) or FAS (Aldrich) at a charge of 0.2% (o.d. pulp) was dissolved in the reserved water and added to the pulp.

The pulp (with pH adjusted and chemicals added) was transferred to a polyethylene bag. The bag was sealed. The pulp inside the sealed bag was homogenized by hand mixing of the pulp from the outside of the bag. The sealed bag was then placed in a water-bath heated to 50°C for 30 minutes. At the end of the pretreatment, the polyethylene bag was cooled in a cold water-bath to room temperature (~20°C). The pulp was diluted with DI H_2O to 1.0% Cs. The pH (end pH) of the pulp slurry was adjusted to 6.0 with 0.1 N H_2SO_4 for pretreatments done at > pH 6.0. The pulp slurry was filtered with the filtrate being recycled once to recover the fines. The same dilution, pH adjustment (if needed) and filtration were then repeated once.

2.4.4 *One-stage "Y + THPS", "Y + $NaBH_4$" or "Y + FAS" bleaching*

For one-stage "Y + THPS" bleaching, the Y bleaching procedure (*see* section 2.3.2) was used except that THPS (Cytec Canada) (0.1-0.4% o.d. pulp) was added to the reserved water after the addition of NaOH and before the addition of sodium hydrosulfite (Y). For one-stage "Y + $NaBH_4$" bleaching, the Y bleaching procedure was used except that $NaBH_4$ (0.1-0.4% o.d. pulp) and the reserved water containing NaOH and Y were added to the pulp simultaneously. For one-stage "Y + FAS" bleaching, the Y bleaching procedure was used except that FAS (0.4% o.d. pulp) and additional NaOH (0.1-0.4% o.d. pulp) were added to the pulp. The pulp initial pH for "Y + FAS" bleaching referred to the pulp pH if Y, FAS and the additional NaOH were not added.

2.4.5 Alkaline hydrogen peroxide bleaching

To a DTPA-pretreated (chelated) TMP or CTMP pulp (12 g o.d.) in a Hobart mixer were added sequentially various amounts of NaOH (1.0-4.0% o.d. pulp); 1.0% (when $H_2O_2 \leq$ 2.0% o.d. pulp) or 3.0% (o.d. pulp) of sodium silicate, Na_2SiO_3; 0.05% (o.d. pulp) of magnesium sulfate, $MgSO_4$; hydrogen peroxide, H_2O_2 (1.0-6.0% o.d. pulp) and DI H_2O to produce, unless otherwise specified, a 20% Cs pulp. The pulp and the bleaching chemicals were mixed for 2-3 minutes in the Hobart mixer, and then transferred to a polyester or polyethylene bag. The air in the headspace of the bag was excluded, and the bag was sealed and immersed in a hot water-bath, unless otherwise specified, at 60°C for 3 hours with manual mixing every hour. At the end of bleaching, the bag was cooled in a cold water-bath to room temperature (~20°C) and enough filtrate was squeezed out by hand and analyzed for end pH. A small amount of the filtrate (~5 mL) was also analyzed for residual peroxide content according to PAPTAC Test Methods, Standard J.16P. The pulp was diluted with DI H_2O to 1.0% Cs. The pH of the pulp slurry was lowered to 6.0 with 6% aqueous SO_2 solution. The pulp slurry was filtered with the filtrate being recycled once to recover the fines, and washed with 400 mL of DI H_2O. The same dilution, pH adjustment, filtration and washing (with 800 instead of 400 mL of DI H_2O) were then repeated once. The filtered pulp was used to make three handsheets (200 g/m^2) according to PAPTAC Test Methods, Standard C.5. The %ISO brightness and CIE b* of the sheets were determined on a Technibrite Micro TB-1C instrument according to PAPTAC Test Methods, Standard E.1, and their average values recorded.

3 Results and Discussion

3.1 Quantification of Blue-stained Chip Content by VIS-NIR on a Rotating Tray

Chip blends with various blue-stained contents were prepared from the blue-stained and the green LPP chips, placed on a laboratory rotating tray with a measured area of ~300 cm^2, and analyzed using Paprican's VIS-NIR spectrometer. Figure 1 (*note*: all Figures begin on page 24) shows the plot of the VIS-NIR predicted blue-stained chip content vs. the actual blue-stained chip content. Excellent linear correlation (with R^2 = ~0.92) was obtained between the actual and the VIS-NIR predicted values. This demonstrates that Paprican's VIS-NIR technique can predict the content of blue-stained chips rather accurately on a rotating tray.

3.2 Quantification of Blue-stained Chip Content by VIS-NIR on a Conveyor

A new set of blended chip samples was then measured on a pilot-plant conveyor system. The predictive model was calculated using half of the available blends and the remaining half of the blends were predicted by the model. The predicted value for each blend was plotted together with the blended values in Figure 2. As can be seen from the plot, Paprican's VIS-NIR spectrometer system (using only 400-1100 nm) can detect variations in blue-stained chip content of the chip blends on a conveyor. The correlation between the predictions and blended values gave a correlation coefficient of r = 0.97 (corresponds

to $R^2 = 0.94$). Such a prediction ability was similar to what was observed in the rotating tray experiment ($R^2 = 0.92$). These results show that Paprican's VIS-NIR spectrometer system has the potential to be used to monitor blue-stained chip content in a mill environment.

3.3 Energy Requirement for and Initial Brightness of the TMP and CTMP Pulps

Table 3 lists the specific refining energy required for the preparation, the Canadian Standard Freeness (CFS), and the ISO brightness of the five TMP and CTMP pulps prepared from chip blends with blue-stained chip contents of 0, 25, 50, 75 and 100%, respectively. The TMP (or CTMP) pulps made from the blue-stained chip blends containing $\geq$ 25% blue-stained chips appeared to require slightly less energy to reach the same freeness than the TMP (or CTMP) pulp from the green chips (chips with 0% blue-stained chip content). In our previous work, we did not find any significant difference in energy requirement for the production of blue-stained and the green TMP (or CTMP) pulps [Hu et al. 2006], due likely to the lightly-infested/stained chips. As expected, the energy consumption to a given freeness for CTMP was higher than that for TMP.

The brightness of 100 or 75% blue-stained TMP (ISO brightness = 55.1%) and that of the 50% blue-stained TMP (ISO brightness = 58.4%) were 5.0 and 1.7 ISO points, respectively, lower than that of the 0% blue-stained (green) TMP (ISO brightness = 60.1%) (Table 3). Interestingly, the brightness of the 25% blue-stained TMP was slightly higher than that of the 0% blue-stained pulp. Previously we did not observe any significant difference in the initial brightness of the blue-stained and the green TMP pulps [Hu et al. 2006], due likely to the lightly-infested/stained chips used. The extent of blue stain in our previous chip sample may have been similar to that of the chip blend with 25% blue-stained chip content used in the present studies.

Overall, the initial brightness of the CTMP pulps was higher than that of the TMP pulps at the same blue-stained chip content (Table 3 and Figure 3). The initial brightness difference between the various blue-stained CTMP and the 0% blue-stained (green) CTMP was still significant. For example, the brightness of the 100% blue-stained CTMP was 4.2 ISO points lower than that of the 0% blue-stained CTMP (Table 3).

Table 3. Specific refining energy requirements for the preparation, the Canadian Standard Freeness (CSF) and the ISO brightness of the various TMP and CTMP pulps.

Pulp	Specific Refining Energy (MJ/kg)	CSF (mL)	ISO Brightness (%)
100% blue-stained TMP	9.78	99	55.1
75% blue-stained TMP	10.50	110	55.1
50% blue-stained TMP	10.59	99	58.4
25% blue-stained TMP	10.47	107	60.9
0% blue-stained TMP	11.07	99	60.1
100% blue-stained CTMP	11.72	92	57.4
75% blue-stained CTMP	12.33	109	58.6
50% blue-stained CTMP	12.42	103	58.5
25% blue-stained CTMP	12.50	110	60.1
0% blue-stained CTMP	12.75	101	61.6

3.4 Effect of Blue Stain Content on Hydrosulfite Bleaching of the TMP Pulps

To study the effect of blue stain content on sodium hydrosulfite (Y) bleaching of the TMP pulps, we first performed the Y bleaching of the 0 and 100% blue-stained TMP pulps, respectively, with various dosages of Y at 5.0% Cs, pulp initial pH ~5.6 and 70°C for 1 h. We found that the 100% blue-stained TMP had a poorer response to Y bleaching than the 0% blue-stained TMP. The initial (unbleached) brightness of the 100% blue-stained TMP was 5.0 ISO points lower than that of the 0% blue-stained TMP (Table 3). However, after bleaching with, for example, 1.0% (o.d. pulp) of Y, the brightness of the Y-bleached, 100% blue-stained TMP was 5.9 ISO points lower than that of the Y-bleached, 0% blue-stained pulp (Figure 4).

Using the method that we described previously [Hu et al. 2006], we found that no blue stain had been removed during Y bleaching of the 100% blue-stained TMP by plotting the CIE b* vs. ISO brightness of the unbleached and the Y-bleached pulps (Figure 5). The presence of blue stain lowered the CIE b* (i.e., the yellowness of the sheet) at the same brightness value, or lowered the ISO brightness at the same CIE b* value [Hu et al. 2006]. Since the data points from Y bleaching of the 100% blue-stained TMP did not move towards the upper right direction and approach the Y bleaching curve of the 0% blue-stained TMP (Figure 5), it could be concluded that no blue stain removal had occurred.

During Y bleaching of the 0 and 100% blue-stained TMP pulps at 5.0% Cs, pulp initial pH ~5.6 and 70°C, we noticed that the pH at the end of bleaching was ~4.5. Such an end pH is lower than the optimal end pH typically found in Y bleaching of mechanical pulps. To see how the various TMP pulps would respond to Y bleaching at higher end pHs, we raised the pulp initial pH from ~5.6 to 7.0 and 8.0, respectively, to give end pHs of ~5.3 and 5.7. We found that the optimal pulp initial pH for the bleaching of the various TMP

pulps was 8.0 with the corresponding optimal end pH being ~5.7 (Figure 6). At such an optimal pH, the 0% blue-stained TMP could be bleached with 1.0% (o.d. pulp) of Y from 60.1 to 69.7% ISO brightness, but the 100% blue-stained TMP could only be bleached from 55.1 to 61.9% ISO brightness. Thus, at such an optimal bleaching pH, the 100% blue-stained TMP had an even poorer bleach response than the 0% blue-stained TMP; the bleached brightness of the 100% blue-stained TMP was 7.8 ISO brightness points lower than that of the 0% blue-stained TMP, compared to 5.9 ISO points lower at non-optimal bleaching pH and 5.0 ISO points lower before bleaching (Table 4). The blue stain in 100% blue-stained TMP not only lowered the unbleached brightness of the TMP pulp, but it also made it more difficult to bleach with Y and introduced an additional brightness ceiling of 7.8 – 5.0 = 2.8 ISO points.

At the optimal bleaching pH, the bleached brightness of the 50 and 25% blue-stained TMP pulps were 3.7 and 1.3 ISO brightness points lower than that of the 0% blue-stained TMP (Table 4). The blue stain in these two pulps introduced additional brightness ceilings of 2.0 and 2.1 ISO points, respectively, because the unbleached brightness of these two pulps were 1.7 ISO points lower and 0.8 ISO point higher than that of the 0% blue-stained pulp. These results were in good agreement with those from our previous studies [Hu et al. 2006]. In our previous studies, the 0% blue-stained TMP could be bleached with 1.0% (o.d. pulp) of Y at buffered pH 6.0 from 55.2 to 62.4% ISO brightness and the lightly blue-stained TMP (the extent of blue stain was not characterized) could only be bleached from 54.9 to 60.0% ISO brightness, giving the additional brightness ceiling / loss of (62.4 – 60.0) – (55.2 – 54.9) = 2.1 ISO points.

Table 4. Unbleached and hydrosulfite-bleached ISO brightness (%) of the various TMP pulps, and the ISO brightness difference (8B[a]) between the various blue-stained TMP and the 0% blue-stained TMP pulps.

TMP	Unbleached brightness (8B)	Bleached brightness with bleaching end pH of ~4.5 (8B)	Bleached brightness with bleaching end pH of ~5.7 (8B)
0% blue-stained	60.1	67.0	69.7
25% blue-stained	60.9 (+0.8)	67.4 (+0.4)	68.4 (-1.3)
50% blue-stained	58.4 (-1.7)	64.8 (-2.2)	66.0 (-3.7)
100% blue-stained	55.1 (-5.0)	61.1 (-5.9)	61.9 (-7.8)

[a]8B = ISO brightness of the unbleached or bleached, blue-stained TMP – ISO brightness of the unbleached or bleached, 0% blue-stained TMP.

In separate experiments, we found that the unusually high pulp initial pH (8.0) needed to obtain an end pH of ~5.7 was due to the use of DI H_2O in the bleaching experiments. When mill or tap water with a higher conductivity than that of DI H_2O was used, the pulp initial pH only needed to be adjusted to ~6.5 to give an end pH of ~5.7 under otherwise same bleaching conditions.

3.5 Evaluation of Various Pretreatments to Overcome the Brightness Ceiling of Hydrosulfite-Bleached, Blue-Stained TMP

In an attempt to develop a cost effective means to overcome the brightness ceiling of the Y-bleached, blue-stained TMP pulps, we pretreated the 100 or 50% blue-stained TMP with caustic (NaOH), sodium sulfite (Na_2SO_3) at various pHs, DTPA, and "DTPA + reducing agent", respectively, prior to Y bleaching. If the fungal melanin pigments are responsible for the blue stain, we may be able to remove some of the blue stain by a caustic pretreatment, or Na_2SO_3 at alkaline pHs where Na_2SO_3 may help preventing the caustic-induced darkening of the pulp during the treatment. If the Fe^{3+}-fungal metabolites are responsible for the blue stain, a DTPA or a "DTPA + reducing agent" chelation pretreatment may remove some of the blue stain. The reducing agent-assisted chelation, "DTPA + reducing agent", has been shown to improve the transition metal (including Fe^{3+}) removal from TMP pulps [Ni et al. 1998].

For the pretreatments with caustic at pH 9.0 and with Na_2SO_3 at pH of 7.6-10.0, only the pretreatment with Na_2SO_3 at pH of 7.6 improved the ISO brightness of the pulp slightly (from 55.1 to 56.1%), but such a slight improvement was not retained after Y bleaching (Table 5). The brightness of the pulp pretreated with NaOH at pH 9.0 and that of the pulp pretreated with Na_2SO_3 at pH 10.0 were 0.6 and 1.0 ISO points lower, respectively, than that of the untreated sample.

Table 5. Effect of caustic, Na_2SO_3 or DTPA pretreatment of 100% blue-stained TMP on its brightness and CIE b* before and after Y bleaching[a].

Pretreatment chemicals and pH	ISO brightness (%) after pretreatment	ISO brightness (%) after pretreatment and Y bleaching
none (control)	55.1 / 13.0	61.9 / 11.5
NaOH at pH 9.0	54.5 / 13.1	60.3 / 11.8
2.0% Na_2SO_3 at pH 7.6	56.1 / 12.9	61.7 / 11.4
2.0% Na_2SO_3 at pH 9.0	55.4 / 12.7	61.0 / 11.5
2.0% Na_2SO_3 at pH 10.0	54.1 / 12.9	61.1 / 11.6
0.5% DTPA at pH 5.0	55.7 / 13.0	61.3 / 11.6
0.5% DTPA at pH 10.0	54.4 / 13.0	60.2 / 11.8

[a]with 1.0% (o.d. pulp) Y at 5% Cs, pulp initial pH 7.0 and 70°C for 1 hour.

DTPA or "DTPA + reducing agent" pretreatment increased the ISO brightness of the 100% blue-stained TMP from 55.1 to 54.4-55.7% (Table 5) or the 50% blue-stained TMP from 58.4 up to 59.6% (Table 6), but only the "DTPA + $NaBH_4$" pretreatment was capable of retaining part of the brightness increase after Y bleaching (Table 6). Inspection of the ISO brightness vs. CIE b* data in Table 5 and Table 6, or plotting the data from the caustic, Na_2SO_3 and DTPA pretreatments of 100% blue-stained TMP (Table 5) on the same graph as those from the unbleached and Y-bleached, 0 and 100% blue-stained TMP pulps indicated that none of these pretreatments had removed any blue stain (Figure 7).

Table 6. Effect of DTPA or "DTPA + reducing agent" pretreatment of 50% blue-stained TMP on its brightness and CIE b* before and after Y bleaching with 1.0% (o.d. pulp) Y at 5% Cs, pulp initial pH 8.0 and 70°C for 1 h.

Pretreatment chemicals and pH	ISO brightness (%) / CIE b* after pretreatment	ISO brightness (%) / CIE b* after pretreatment and Y bleaching
none (control)	58.4 / 13.0	66.0 / 11.2
0.5% DTPA at pH 6.0	59.0 / 13.0	66.1 / 11.4
"0.5% DTPA + 0.2% Y" at pH 6.0	58.9 / 13.1	65.8 / 11.4
"0.5% DTPA + 0.2% $NaBH_4$" at pH 8.0	59.6 / 12.8	66.6 / 11.2
"0.5% DTPA + 0.2% FAS" at pH 8.0	58.8 / 13.1	66.3 / 11.4

Pretreatments of the 100% blue-stained TMP with a proprietary Fe-specific, chelating agent or "Fe-specific chelating agent + reducing agent" (data not shown) did not lead to any detectable removal of blue stain either. These results, together with those from the DTPA and "DTPA + reducing agent" pretreatments, indicate that the Fe^{3+}-fungal metabolites are unlikely responsible for the blue stain. The fungal melanin pigments are more likely responsible for the blue stain. We did not study the caustic (NaOH) or Na_2SO_3 pretreatments at pH $\geq$ 9.0 or 10.0 for the possible removal of fungal melanin pigments because we found that alkaline-induced darkening of the pulps had already occurred at pH 9.0 (for NaOH pretreatment) or 10.0 (for Na_2SO_3 pretreatment) (Table 5).

3.6 Evaluation of One-stage "Y + THPS (or $NaBH_4$ or FAS) as a Means to Overcome the Brightness Ceiling of Y-Bleached, Blue-Stained TMP

In another attempt to develop a cost effective means to overcome the brightness ceiling of the Y-bleached, blue-stained TMP pulps, we performed one-stage "Y + THPS" "Y + $NaBH_4$" and "Y + FAS" bleaching of the 100% blue-stained TMP, respectively, with 1.0% (o.d. pulp) of Y and $\leq$ 0.4% (o.d. pulp) of THPS, $NaBH_4$, or FAS at various pulp initial pHs. If such one-stage bleaching is capable of overcoming the brightness ceiling, it will be easy to implement in the mills by adding THPS, $NaBH_4$, or FAS along with Y to the existing mill Y bleaching processes. We found that all the one-stage "Y + reducing agent" bleaching improved the brightness noticeably with "1.0% Y + 0.1 or 0.2% $NaBH_4$" being the most effective (Table 7) in terms of brightness gain/reducing chemical cost. The current cost of $NaBH_4$/kg is lower than that of THPS or FAS. The brightness of the 100% blue-stained TMP bleached with "1.0% Y + 0.2% $NaBH_4$" was 1.2 ISO points higher than that of the pulp bleached with Y under the most optimal conditions (1.0% Y at pulp initial pH of 7.0 or 8.0) (Table 7).

Table 7. ISO brightness and CIE b* of the 100% blue-stained TMP (55.1% ISO brightness) bleached with Y, "Y + THPS (or $NaBH_4$ or FAS)" at 5% Cs and 70°C for 1 hour, respectively.

Bleaching chemical	Pulp initial pH	ISO brightness (%) / CIE b* after bleaching
1.0% Y	5.7	61.1 / 11.7
1.2% Y	5.7	60.5 / 11.8
1.0% Y	7.0 or 8.0	61.9 / 11.5
1.0% Y + 0.1% THPS	5.5	62.3 / 11.4
1.0% Y + 0.1% $NaBH_4$	8.0	62.6 / 11.1
1.0% Y + 0.2% $NaBH_4$	8.0	63.1 / 10.9
1.0% Y + 0.4% $NaBH_4$	8.0	62.7 / 10.3
1.0% Y + 0.4% FAS + 0.1% NaOH	5.5	61.5 / 11.7
1.0% Y + 0.4% FAS + 0.2% NaOH	5.5	62.6 / 11.4
1.0% Y + 0.4% FAS + 0.4% NaOH	5.5	62.5 / 11.5

Plotting the data of the 100% blue-stained TMP bleached with "1.0% Y + 0.1% THPS", "1.0% Y + 0.1-0.2% $NaBH_4$" and "1.0% Y + 0.4% FAS" on the same graph as those from the unbleached and Y-bleached, 0 and 100% blue-stained TMP pulps (Figure 8) indicated that the additional brightness gain from "1.0% Y + 0.1-0.2% $NaBH_4$" over 1.0% Y bleaching was due mainly to the further bleaching of lignin, but the additional gain from "1.0% Y + 0.1% THPS" or "1.0% Y + 0.4% FAS" bleaching was due at least partly to blue stain removal.

If the additional brightness gain from "1.0% Y + 0.2% $NaBH_4$" bleaching of the 100% blue-stained TMP was indeed due to the further bleaching of lignin, one would expect similar, additional brightness gains from such bleaching of other blue-stained TMP pulps as well as the green (0% blue-stained) TMP. More importantly, one would be able to overcome the brightness ceiling of Y-bleaching of the 25% blue-stained TMP since the Y-bleached brightness of this pulp (68.4% ISO) was only 1.3 ISO points lower than that of the Y-bleached, 0% blue-stained TMP (69.7% ISO) (Table 4). Indeed, this was found to be the case. Bleaching of the 0, 25 and 50% blue-stained TMP pulps with "1.0% Y + 0.2% $NaBH_4$" gave additional brightness gains of 1.3, 1.7 and 1.4 ISO points, respectively, over the Y bleaching of the pulps (Table 8). The ISO brightness of the 25% blue-stained TMP bleached with "1.0% Y + 0.2% $NaBH_4$" was 70.1% which was slightly higher than that of the 0% blue-stained TMP (green TMP) bleached with 1.0% Y. Thus, a cost effective means to overcome the brightness ceiling of the Y-bleached, blue-stained TMP is to use a one-stage, "1.0% Y + 0.2% $NaBH_4$" bleaching, if the TMP is made from a chip furnish containing $\leq$ 25% blue-stained chip contents.

Table 8. Additional brightness gain from "1.0% Y + 0.2% $NaBH_4$" bleaching over 1.0% Y bleaching for the 0, 25 and 50% blue-stained TMP pulps; all the bleaching was done at 5% Cs, pulp initial pH 8.0 and 70°C for 1 hour.

TMP	ISO brightness (%) after 1.0% Y bleaching	ISO brightness (%) after "1.0% Y + 0.2% $NaBH_4$" bleaching	Additional brightness gain (ISO point)
0% blue-stained	69.7	71.0	+1.3
25% blue-stained	68.4	70.1	+1.7
50% blue-stained	66.0	67.4	+1.4

3.7 Effect of Blue Stain Content on Alkaline Hydrogen Peroxide Bleaching of the TMP Pulps

To study the effect of blue stain content on alkaline hydrogen peroxide (P) bleaching of the TMP pulps, we first preformed the P bleaching on 0, 50 and 100% blue-stained, DTPA-chelated TMP with various dosages of the P bleaching chemicals at 20% Cs and 60°C for 3 hours. We found that the brightness the P-bleached TMP pulps depended not only on the P bleaching chemical dosages, but also on the blue stain content [Table 9, Figure 9]. The higher the blue stain content and the lower the bleaching chemical dosage, the more difficult it is to bleach the blue-stained TMP close to the brightness level of the 0% blue-stained TMP. For example, at 1.0% H_2O_2 dosage, the 100 and 50% blue-stained TMP pulps could only be bleached to ISO brightness values of 63.0 and 66.1%, respectively, which were 6.3 and 3.2 ISO points lower than the ISO brightness of the 1.0% H_2O_2-bleached, 0% blue-stained TMP (69.3% ISO) (

Table 9). At 5.0% H_2O_2 dosage, the 100 and 50% blue-stained TMP pulps could be bleached to ISO brightness values of 75.5 and 76.0%, respectively, which were 1.4 and 0.9 ISO points lower than the ISO brightness of the 5.0% H_2O_2-bleached, 0% blue-stained TMP (76.9% ISO).

Table 9. ISO brightness (%) and CIE b* of the 0, 50 and 100% blue-stained, DTPA-chelated TMP pulps before and after alkaline hydrogen peroxide bleaching[a] at 20% Cs and 60°C for 3 hours; bleaching end pH values are shown in bracket.

H_2O_2 / NaOH (% o.d. pulp)	Brightness / CIE b* for 0% blue-stained TMP {end pH}	Brightness / CIE b* for 50% blue-stained TMP {end pH}	Brightness / CIE b* for 100% blue-stained TMP {end pH}
none	60.1 / 12.8	58.4 / 13.0	55.1 / 13.0
1.0 / 1.0	69.3 / 12.3 {7.8}	66.1 / 11.5 {7.5}	63.0 / 11.6 {7.5}
1.5 / 1.5	71.3 / 11.9 {7.6}	67.6 / 11.2 {7.8}	65.2 / 11.3 {7.6}
2.0 / 2.0	72.7 / 11.4 {8.2}	69.6 / 10.8 {7.8}	66.0 / 11.2 {n.a.}[b]
4.0 / 3.0	76.0 / 10.3 {9.6}	73.8 / 10.5 {9.3}	73.3 / 10.6 {9.4}
5.0 / 3.5	76.9 / 9.7 {9.9}	76.0 / 10.0 {9.5}	75.5 / 10.1 {9.6}
6.0 / 4.0	77.9 / 9.2 {10.2}	77.4 / 9.3 {9.8}	76.6 / 9.6 {9.9}

[a] *see* Material and Methods section for sodium silicate and magnesium sulfate dosages for the bleaching experiments; [b] end pH data not available.

When we plotted data of CIE b* vs. the ISO brightness of the unbleached and various P-bleached pulps (Figure 10) and analysed the data using our method of determining lignin bleaching vs. blue stain removal described earlier, we found that bleaching of the 100 and 50% blue-stained pulps at ≤ 2.0% (o.d. pulp) of H_2O_2 (the data points at ISO brightness of ≤ 69.6%) did not remove the blue stain to any significant extent, but bleaching of the pulps at ≥ 4.0% (o.d. pulp) of H_2O_2 removed most of the blue stain. The removal of blue stain coincided with an increase of peroxide bleaching end pH from 7.5-7.8 to 9.3-9.9 (

Table 9). These results suggest that fungal melanin pigments are responsible for the blue stain, because melanins in general are soluble in strong alkali and can be discoloured by reaction with H_2O_2 (Nicolaus 1968; Zink and Fengel 1988). They also show that for effective removal of the blue stain, a higher initial H_2O_2 concentration and/or higher peroxide bleaching end pH are/is required. The initial H_2O_2 concentration for the bleaching with 4.0% (o.d. pulp) of H_2O_2 at 20% Cs is 10 g/L, compared to 5.0 g/L for the bleaching with 2.0% (o.d. pulp) of H_2O_2 at 20% Cs.

To determine if the initial H_2O_2 concentration for alkaline hydrogen peroxide (P) bleaching played any role in blue stain removal, we performed additional P-bleaching on the 0 and 100% blue-stained TMP pulps with fixed, 5.0% (o.d. pulp) of H_2O_2 and 4.0% (o.d. pulp) of NaOH at 60°C and 10, 20 and 25% Cs, respectively, for 3 hours. If the initial H_2O_2 concentration played a role in blue stain removal, the brightness difference between the P-bleached, 0% blue-stained and the P-bleached, 100% blue-stained TMP pulps would be the largest at 10% Cs with initial H_2O_2 concentration of ~5.6 g/L, while the difference between the two bleached pulps would be the smallest at 25% Cs with initial H_2O_2 concentration of ~16.7 g/L. Plots of the data of ISO brightness of the P-bleached pulps vs. bleaching Cs from these additional bleaching experiments (Figure 11) showed that the brightness difference between the P-bleached, 0% blue-stained and the P-bleached, 100% blue-stained pulps was independent of the Cs. Thus, the higher bleaching end pH, not the higher initial H_2O_2 concentration, was responsible for the blue stain removal in the bleaching of the blue-stained TMP pulps at ≥ 4.0% (o.d. pulp) of H_2O_2.

3.8 Overcoming the Brightness Ceiling of Peroxide-Bleaching of the 50% Blue-Stained TMP by Raising the Bleaching End pH

The demonstration of the ability of high peroxide bleaching end pH (9.3-9.9) to remove blue stain prompted us to examine the possibility of bleaching the blue-stained TMP pulps to higher brightness by raising the end pH further. To this end, we performed the bleaching of the 0, 50 and 100% blue-stained, DTPA-chelated TMP pulps with 6.0% H_2O_2 and 4.5 and 5.0% NaOH, respectively, at 20% Cs and 60°C for 3 hours. Table 10 lists the values of the ISO brightness and the end pH for the P-bleached pulps, along with those for the pulps bleached with 6.0% H_2O_2 and 4.0% NaOH (*see*

Table 9) and Figure 12 plots the ISO brightness vs. NaOH dosage. Increasing the dosage of NaOH from 4.0 to 4.5% (o.d. pulp) (or the end pH from 9.8 to 10.0 or 10.1) allowed the P-bleaching of the 50% blue-stained TMP pulp to the same ISO brightness as the P-bleaching of the 0% blue-stained TMP. However, the brightness of the P-bleached, 100% blue-stained TMP was still lower than that of the P-bleached, 0% blue-stained

TMP by 1.0 ISO point (Table 10). Further increase of the dosage of NaOH to 5.0% decreased the brightness of all the three pulps slightly, due likely to the increased, alkali-induced darkening of the pulp during bleaching.

Table 10. Effect of NaOH charge and end pH on alkaline peroxide bleaching[a] of 0, 50 and 100% blue-stained, DTPA-chelated TMP pulps with 6.0% (o.d. pulp) of H_2O_2 at 20% Cs and 60°C for 3 hours.

NaOH (% o.d. pulp)	ISO brightness (%) for 0% blue-stained TMP {end pH}	ISO brightness (%) for 50% blue-stained TMP {end pH}	ISO brightness (%) for 100% blue-stained TMP {end pH}
4.0	77.9 {10.2}	77.4 {9.8}	76.6 {9.9}
4.5	78.7 {10.1}	78.8 {10.0}	77.7 {10.1}
5.0	78.5 {10.3}	78.6 {10.3}	77.6 {10.1}

[a]*see* Material and Methods section for sodium silicate and magnesium sulfate charges for the bleaching experiments.

The removal of the blue stain or the complete and partial overcoming of the brightness ceiling of the P-bleached, 50 and 100% blue-stained TMP pulps may be due to the brightening of the blue stain and/or to the degradation/dissolution of the blue stain. Dissolution of the blue stain into the bleaching medium may cause changes to the effluent quality such as chemical oxygen demand (COD) and biological oxygen demand (BOD). Preliminary results from the analyses of the filtrates from P-bleaching of the 0, 50 and 100% blue-stained TMP pulps with 6.0% H_2O_2 and 4.5% NaOH showed that there was a significant increase in the COD content, but a small decrease in the BOD content of the filtrates from the bleaching of the blue-stained TMP pulps (Table 11). Further studies are required to confirm the contribution of dissolved blue stain to the COD and BOD contents of the bleaching filtrates/effluents.

Table 11. COD and BOD of the filtrates from alkaline hydrogen peroxide bleaching[a] of the TMP pulps with 6.0% H_2O_2 and 4.5% NaOH at 20% Cs and 60°C for 3 hours.

TMP	ISO brightness (%) of the bleached pulp	COD (kg/ton pulp)	BOD (kg/ton pulp)
0% blue-stained	78.7	64.1	35.0
50% blue-stained	78.8	74.2	31.4
100% blue-stained	77.7	80.1	32.8

[a]*see* Material and Methods section for sodium silicate and magnesium sulfate charges for the bleaching experiments.

In another effort to bleach the 100% blue-stained, DTPA-chelated TMP to the same brightness level as the 0% blue-stained TMP, we studied the peroxide bleaching of 0 and 100% blue-stained TMP pulps at an optimal end pH (optimal H_2O_2/NaOH ratio) and at temperatures higher than 60°C and for various times. Typically, a shorter bleaching time needs to be used for the bleaching of mechanical pulps at a higher bleaching temperature to minimize the heat-induced darkening of the pulps. We found that one additional ISO brightness point could be obtained on the P-bleached, 100% blue-stained TMP when the bleaching temperature was raised from 60 to 80°C and the bleaching time was reduced

from 3 to 2 hours. The brightness of the 100% blue-stained TMP bleached with 5.0% H_2O_2 under optimal conditions (end pH, temperature and time) (77.6% ISO) was practically identical to that of the 0% blue-stained TMP bleached at 60°C for 3 hours (77.7% ISO), but it was still 0.8 ISO point lower than that of the 0% blue-stained TMP bleached under optimal conditions of 70°C for 3 hours (Table 12 and Figure 13).

Table 12. ISO brightness (%) of the 0 and 100% blue-stained, DTPA-chelated TMP pulps bleached with 5.0% H_2O_2 and 4.5% NaOH at 20% Cs and various temperatures for various times[a].

Temperature (°C) / time (h)	ISO brightness (%) for the 0% blue-stained TMP {end pH}	ISO brightness (%) for the 100% blue-stained TMP {end pH}
60 / 3	77.7 {10.8}	76.6 {10.9}
70 / 3	78.4 {10.5}	77.3 {10.3}
80 / 3	78.2 {10.1}	77.2 {10.2}
80 / 2	78.1 {10.2}	77.6 {10.2}
90 / 1	76.5 {9.8}	74.2 {9.9}
90 / 0.5	75.5 {10.9}	75.0 {10.9}
90 / 0.25	75.3 {11.0}	72.5 {10.9}

[a] *see* Material and Methods section for sodium silicate and magnesium sulfate charges for the bleaching experiments.

3.9 Effect of Blue Stain Content on Alkaline Hydrogen Peroxide Bleaching of the CTMP Pulps

In our previous work, we found that CTMP prepared from blue-stained LPP chips (the extent of blue stain was not characterized) responded to alkaline hydrogen peroxide bleaching better than CTMP prepared from the green LPP chips [Hu et al. 2006]. To see how the more intensively blue-stained CTMP from our current studies responded to alkaline hydrogen peroxide bleaching in comparison with the 0% blue-stained CTMP (green CTMP). We bleached the 0 and 100% blue-stained, DTPA-chelated CTMP pulps with various alkaline hydrogen peroxide at 20% Cs and 60°C for 3 h. Similar to the TMP pulps, the brightness difference between the P-bleached, 0% blue-stained CTMP and the P-bleached, 100% blue-stained CTMP became smaller at a higher alkaline hydrogen peroxide dosage ($\geq$ 4.0% H_2O_2 o.d. pulp) or a higher end pH ($\geq$ 10.4) (Table 13, Figure 13) due to the increased removal of the blue stain (Figure 14). Different from the TMP pulps, however, the 100% blue-stained CTMP could be bleached to the same brghtness level as that of the 0% blue-stained CTMP with $\geq$ 5.0% (o.d. pulp) of H_2O_2 (Table 13, Figure 13) due to the complete removal of the blue stain. The complete removal of the blue stain in the 5.0 or 6.0% H_2O_2-bleached, 100% blue-stained CTMP was deduced from the practically identical ISO brightness and CIE b* of such a bleached pulp to those of the P-bleached, 0% blue-stained CTMP (Table 13, Figure 14). The higher reactivity of the blue stain in the CTMP pulp towards alkaline hydrogen peroxide than that of the blue stain in the TMP pulps is likely due to the sulfonation of the blue stain. The results from the P-bleaching of the blue-stained CTMP further suggest that the fungal melanin pigments, not the Fe^{3+}-fungal metabolites, are responsible for the blue stain.

Table 13. ISO brightness (%) and CIE b* of the 0 and 100% blue-stained, DTPA-chelated CTMP pulps before and after alkaline hydrogen peroxide bleaching[a] at 20% Cs and 60°C for 3 hours; bleaching end pH values are shown in bracket.

H_2O_2 / NaOH (% o.d. pulp)	Brightness / CIE b* for 0% blue-stained CTMP {end pH}	Brightness / CIE b* for 100% blue-stained CTMP {end pH}
none	62.5 / 13.0	57.6 / 12.5
2.0 / 2.0	74.4 / 11.0 {9.3}	72.0 / 10.5 {9.1}
4.0 / 3.0	77.3 / 9.6 {10.5}	76.7 / 9.5 {10.4}
5.0 / 3.5	77.8 / 9.1 {10.5}	77.8 / 9.0 {10.5}
5.0 / 4.0	78.0 / 9.1 {10.7}	77.6 / 9.0 {11.0}
6.0 / 4.0	78.4 / 9.0 {10.8}	78.4 / 8.8 {10.8}

[a]*see* Material and Methods section for sodium silicate and magnesium sulfate dosages for the bleaching experiments.

Our results show that CTMP mills that use high dosages of alkaline hydrogen peroxide (≥ 5.0% H_2O_2) in their bleaching processes are not expected to have any problems reaching brightness targets for their pulps made from chip furnishes containing high level of blue stain. In addition, CTMP mills that use medium dosages of alkaline hydrogen peroxide (2.0 – 4.0% H_2O_2) would need less extra bleaching chemicals to achieve brightness targets for their bleached pulps made from blue-stained chips than TMP mills.

3.10 Characterization of the Chemical Compositions of the Blue-stained Chips

As an effort to determine the chemical compositions of the blue stain and in collaboration with Dr. John Kadla at the University of British Columbia Department of Wood Science, samples of the green (referred to as healthy) and the blue-stained (referred to as infected) chips were fractionated by successive extractions with acetone, dioxane (after ball milling) and DMSO and characterized (with or without acetylation) by a number of advanced analytical techniques (*see* Section 2.1). The blue-stained chips were found to have a lower content of acetone extractives, due likely to the preferential metabolism of nonstructural wood components such as triglycerides by the blue-staining fungi. Indeed, ^{1}H, ^{13}C and HSQC NMR spectra of the extractives from the blue-stained (referred to as infected) chips showed a drastic decrease of the triglyceride signal intensity, compared with the specctra of the extractives from the green (referred to as healthy) chips (Figure 15 and Figure 16).

Elemental, Klason lignin and carbohydrate analyses, as well as FTIR, ^{1}H, ^{13}C and HSQC NMR analyses of the milled wood lignin (MWL), lignin-carbohydrate complex (LCC), the LCC-rich and LCC-poor soluble fractions showed no significant differences in the chemical compositions of the green and the blue-stained samples. SEC chromatograms of the acetylated (MWL) and LCC-rich fractions were also the same for the green and the blue-stained chips. However, the LCC-poor fraction from the blue-stained chips was found to contain slightly more low-molecular weight UV-absorbant material at 310 – 450

nm (Figure 17). Further studies of this fraction may lead to the identification of the chemical structures of the blue stain, or fragments of the blue stain.

4 Conclusions

The initial brightness of thermomechanical pulps (TMPs) and chemithermomechanical pulp (CTMP) made from chip blends containing mountain pine beetle-infested (kill date = 2-3 years), blue-stained, lodgepole pine (LPP) chips is up to 5.0 ISO points lower than that of the pulps made from the green LPP chips; the higher the blue-stained chip content in the chip blends, the lower the initial brightness of the pulps. Paprican's VIS-NIR technique is capable of predicting the blue-stained chip content in the chip blends accurately with a correlation coefficient of $R^2 \geq 0.92$ on a laboratory rotating trap or on a pilot-plant conveyor.

Thermomechanical pulps made from chip blends with various blue-stained chip contents all have lower sodium hydrosulfite (Y) bleaching response than TMP pulp made from the green chips; an additional brightness ceiling of 2.0 - 2.8 ISO points are introduced during Y bleaching of the blue-stained pulps, making the brightness of the Y-bleached, blue-stained TMP up to 7.8 ISO points lower than the Y-bleached, green TMP.

A method to overcome the brightness ceiling of Y-bleached TMP made from chip blends with 25% blue-stained chip content has been developed. The method involves the addition of 0.2% (o.d. pulp) of sodium borohydride to Y bleaching in one-stage and it works by further bleaching of the lignin instead of removing the blue stain. None of the reducing agents (sodium borohydride, THPS and FAS) is capable of overcoming the brightness ceiling of TMP pulps made from chip blends with ≥ 50% blue-stained chips. Pretreatment of the blue-stained TMP pulps with caustic at pH 9.0 or sodium sulfite at pH ≤ 10.0 prior to Y bleaching provides none or little additional brightness gain to the Y-bleached, blue-stained pulps.

A high bleaching end pH in alkaline hydrogen peroxide bleaching has been discovered to be capable of removing most or all of the blue stain in TMP pulps made from chip blends with 50-100% blue-stained chip contents. Thus, optimal peroxide bleaching conditions (for example $H_2O_2 \geq 5.0\%$ o.d. pulp, end pH = ~10.0) have been identified to allow the bleaching of the TMP pulp made from chip blends with 50% blue-stained chip content to the same brightness as the bleaching of the pulp from the green chips. However, the brightness of the TMP made from 100% blue-stained chips and bleached with alkaline hydrogen peroxide under optimal bleaching conditions ($H_2O_2 \geq 5.0\%$, end pH ~10.0-10.2 and 80°C) is still 0.8 ISO points lower than that of the TMP made from the green chips bleached with alkaline hydrogen peroxide under optimal conditions.

Chemithermomechanical pulp made from the 100% blue-stained chips can be bleached with alkaline hydrogen peroxide to the same brightness as CTMP made from the green chips under optimal bleaching conditions ($H_2O_2 \geq 5.0\%$, end pH 10.5-11.0). This has been shown to be due to the complete removal of the blue stain under such optimal

bleaching conditions.

The blue stain in the sapwood of mountain pine beetle-infested LPP appears to be the fungal melanin pigments based on our bleaching data. The blue stain chips have lower triglyceride content than the green chips. The DMSO-soluble, lignin-carbohydrate-complex-poor fraction from the blue-stained chips appears to contain the blue stain as only this fraction shows significant chemical difference from that of the green chips; its SEC chromatogram contains slightly more low-molecular weight UV-absorbing material.

5 Acknowledgements

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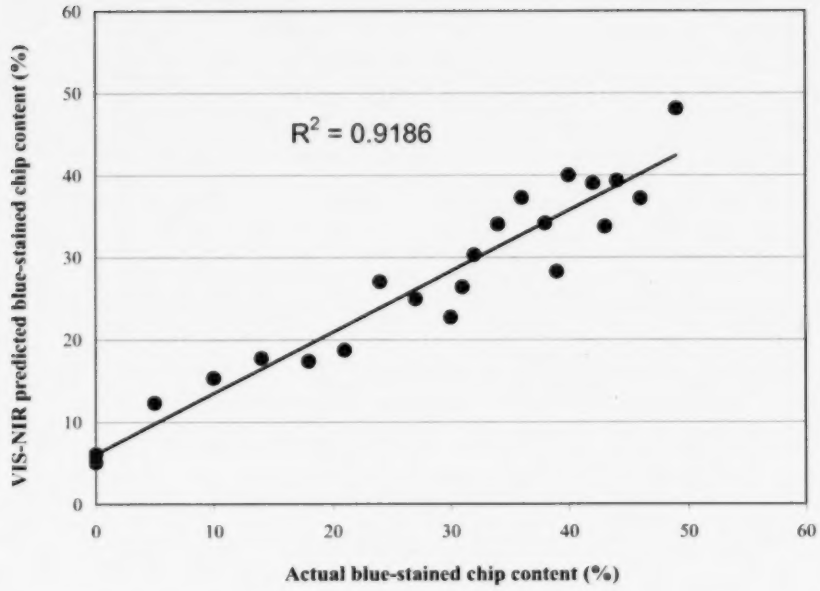

Figure 1. VIS-NIR predicted vs. actual blue-stained chip content (%).

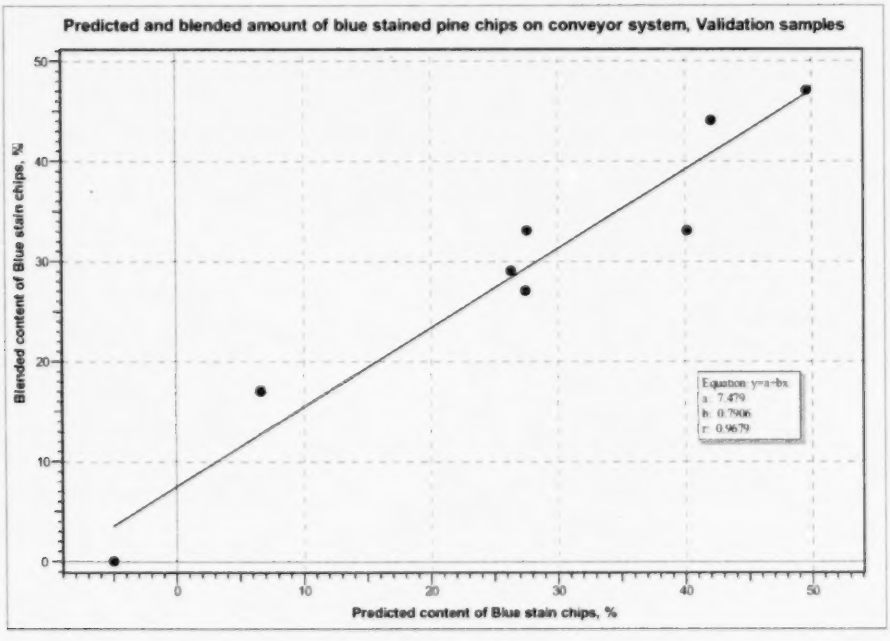

Figure 2. Bended blue-stained chip content vs. VIS-NIR-predicted, blue-stained chip content measured on a conveyor for 8 validation blends.

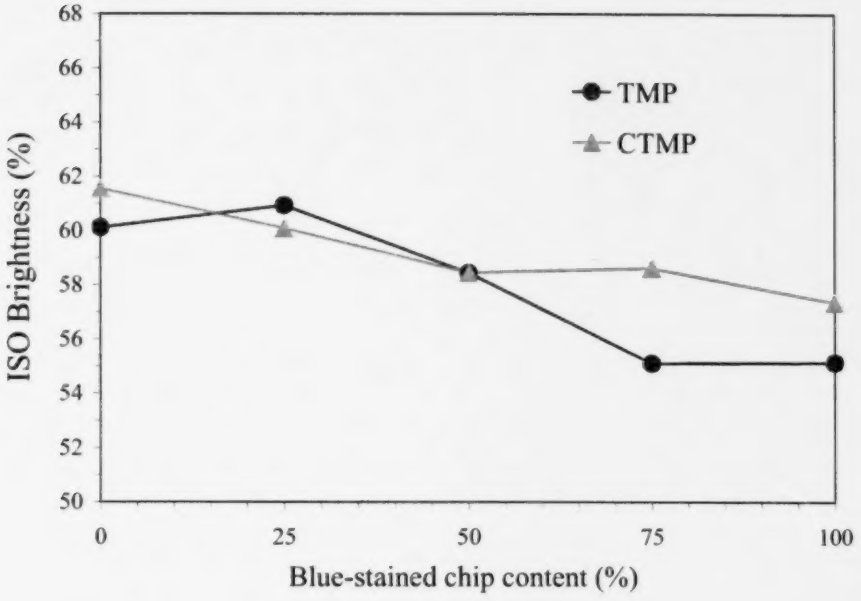

Figure 3. Effect of blue-stained chip contents on the initial brightness of the TMP and CTMP pulps.

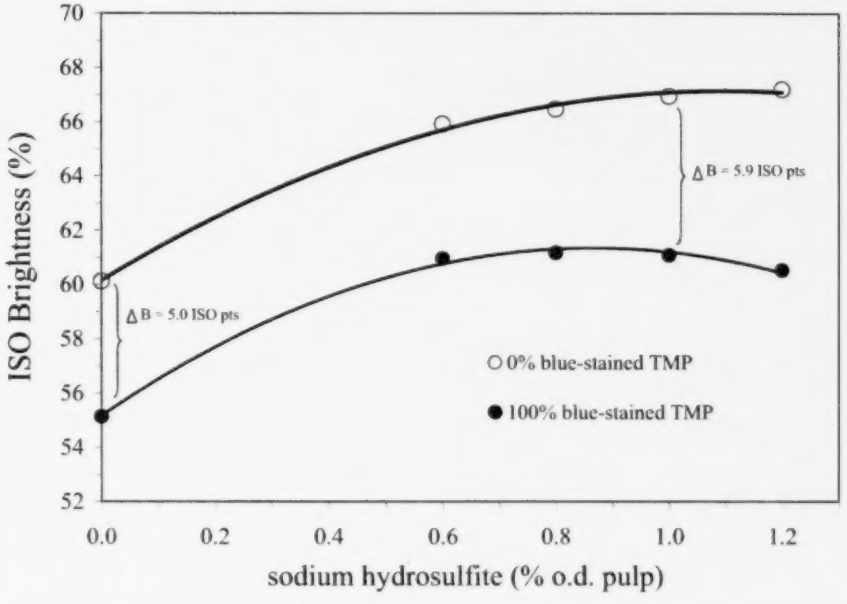

Figure 4. Bleaching of the 0% and 100% blue-stained TMP pulps with various dosages of sodium hydrosulfite at 5.0% Cs, pulp initial pH ~5.6 and 70°C for 1 h.

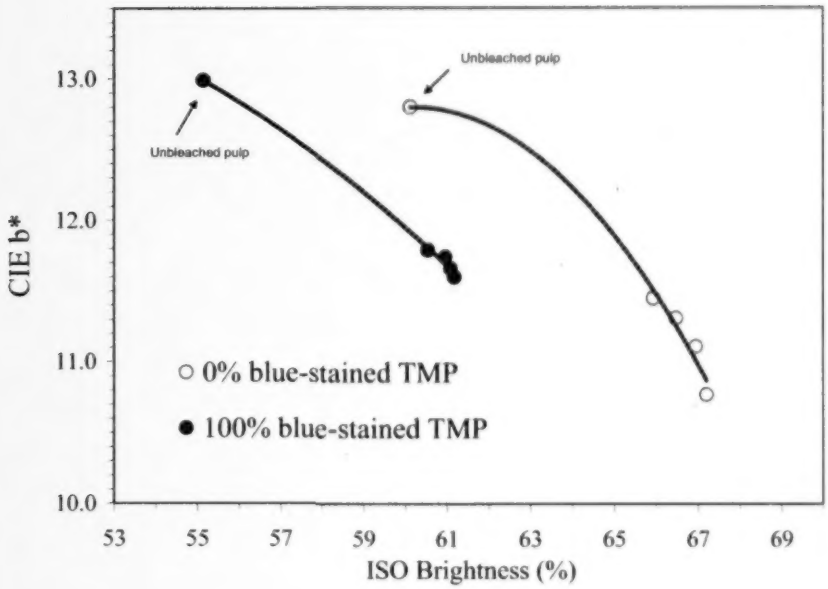

Figure 5. CIE b* vs. ISO brightness of the unbleached and the hydrosulfite-bleached, 0% and 100% blue-stained TMP pulps.

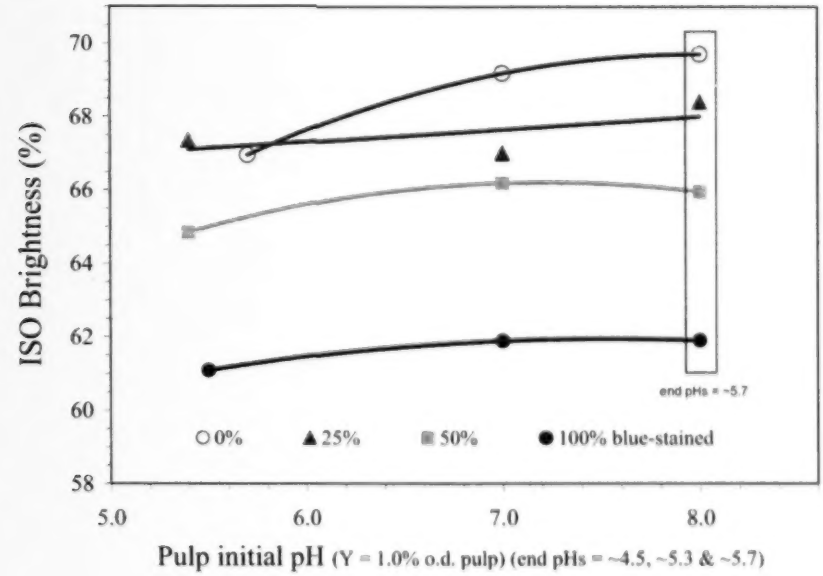

Figure 6. Response of the 0% blue-stained and various blue-stained TMP pulps to sodium hydrosulfide leaching at various pulp initial pHs (or end pHs).

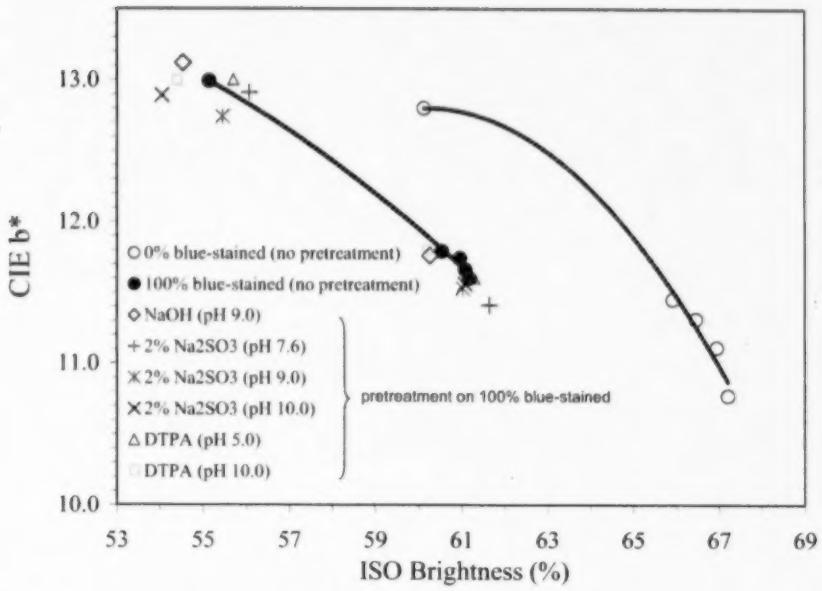

Figure 7. CIE b* vs. ISO brightness of 0% and 100% blue-stained TMP pulps, and the various pretreated 100% blue-stained TMP pulps; both unbleached and Y-bleached data are shown.

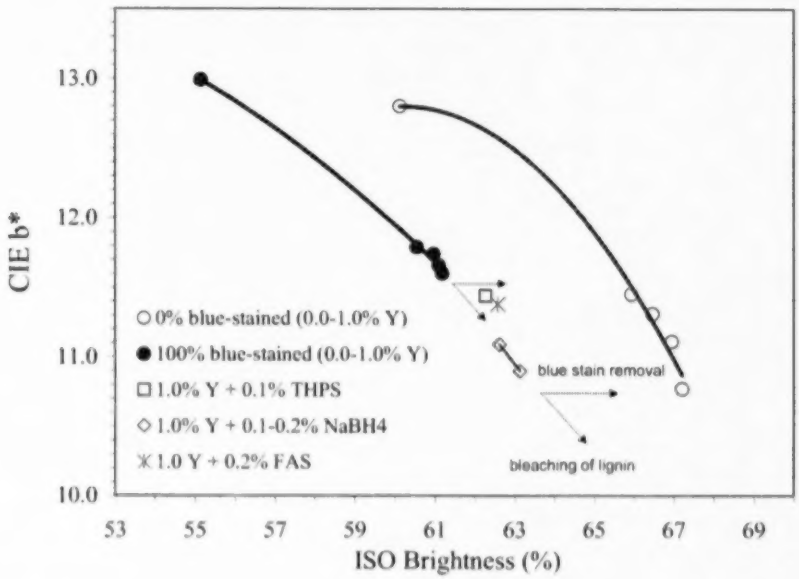

Figure 8. CIE b* vs. ISO brightness of the unbleached and Y-bleached, 0% and 100% blue-stained TMP pulps, and of the various one-stage "Y + reducing agent"-bleached, 100% blue-stained TMP pulps.

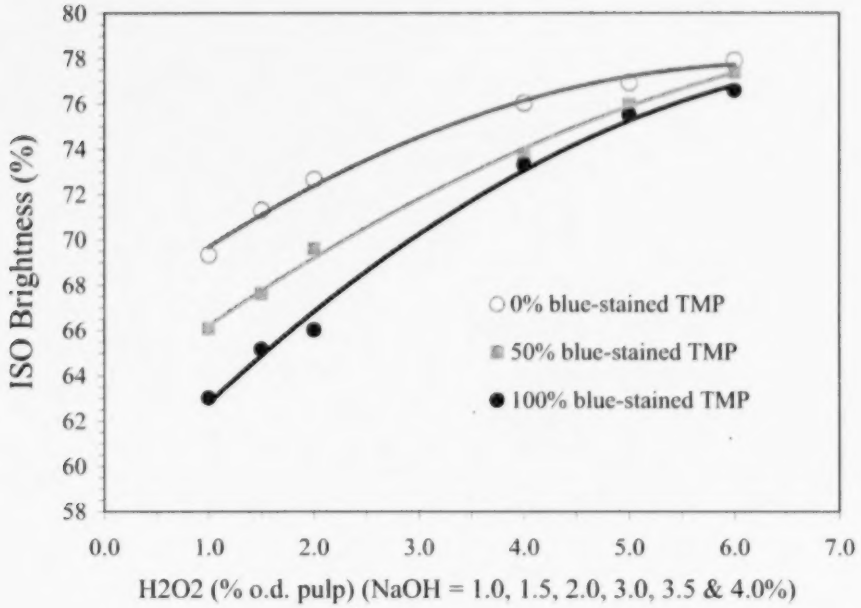

Figure 9. Effect of hydrogen peroxide and blue stain content on ISO brightness of the alkaline hydrogen peroxide-bleached TMP pulps.

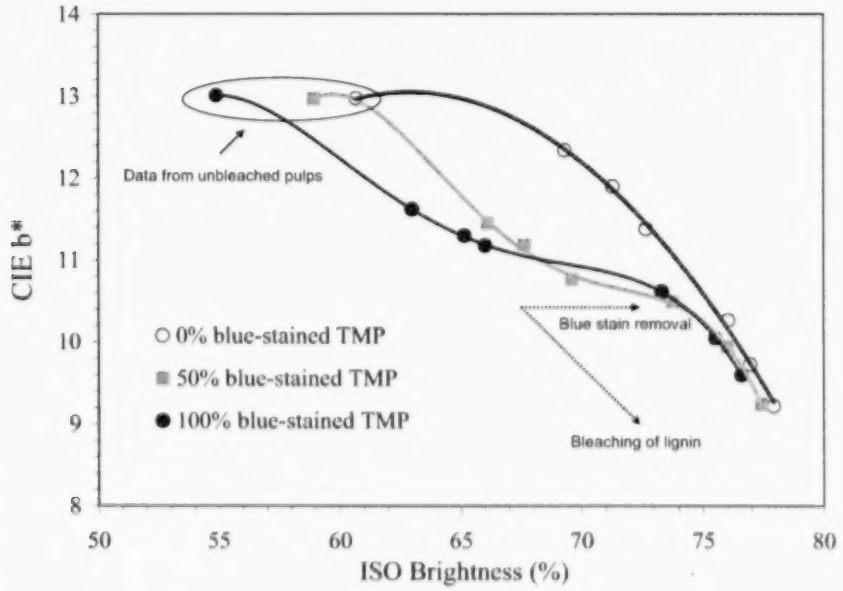

Figure 10. CIE b* vs. ISO brightness of the unbleached TMP pulps and the pulps bleached with various amounts of alkaline hydrogen peroxide.

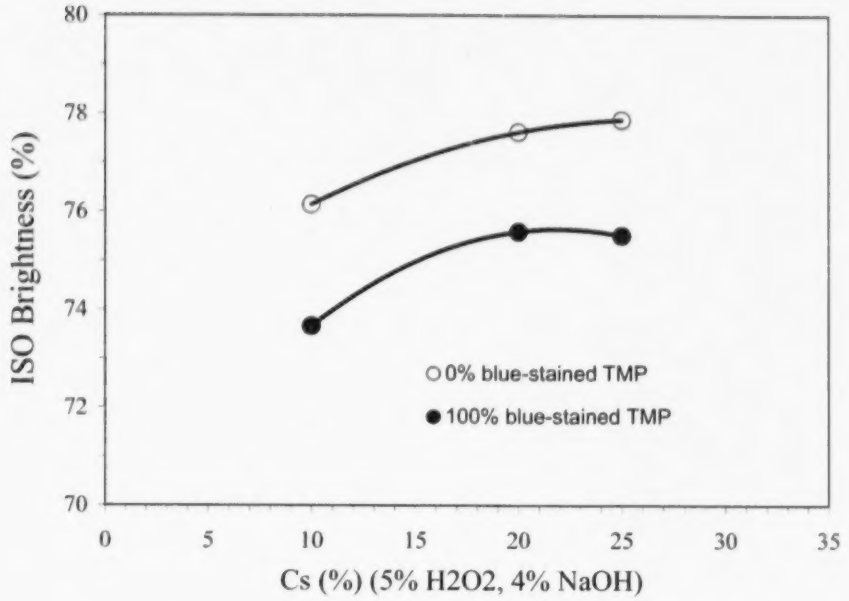

Figure 11. Effect of bleaching consistency (Cs) on the bleaching of the 0 and 100% blue-stained TMP pulps with 5% H_2O_2 and 4% NaOH.

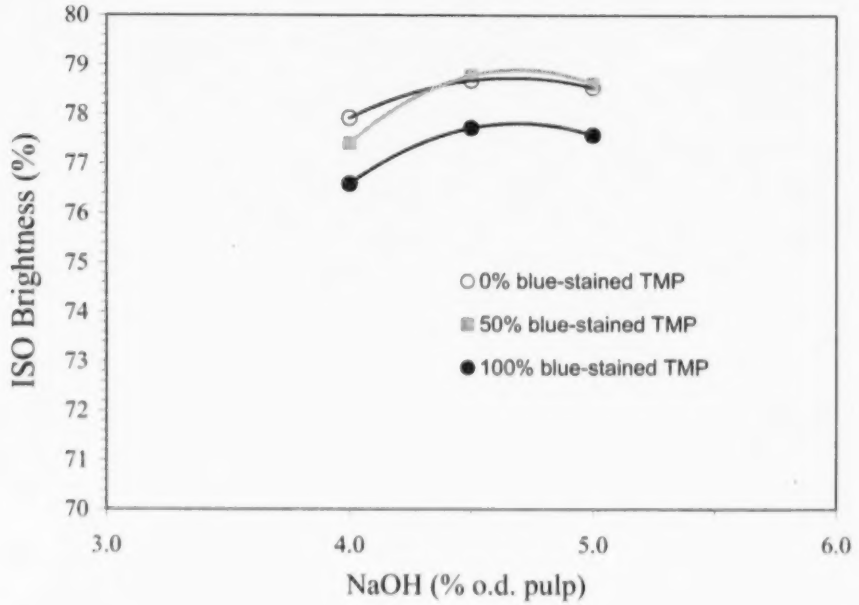

Figure 12. Effect of caustic dosage and blue stain content on the bleaching of the TMP pulps with 6% H_2O_2.

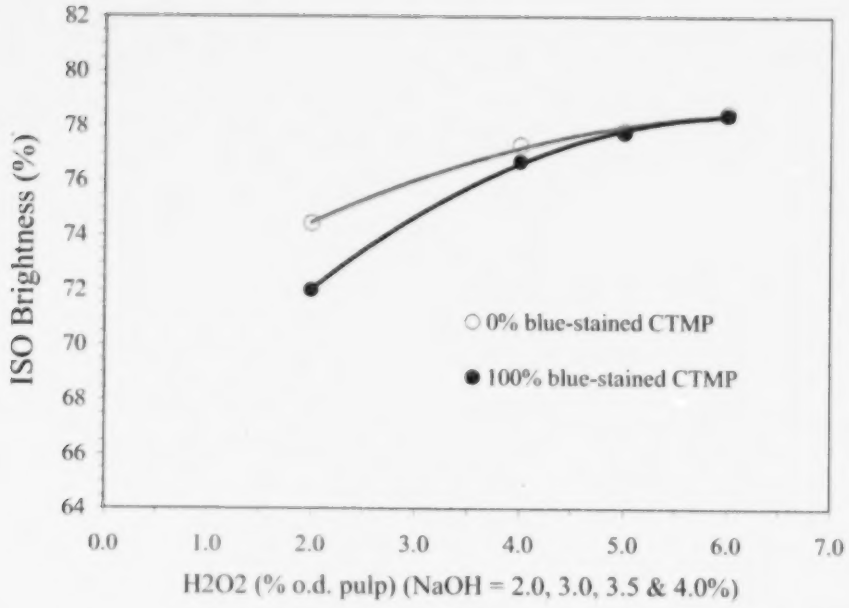

Figure 13. Effect of hydrogen peroxide and blue stain content on ISO brightness of the alkaline hydrogen peroxide-bleached CTMP pulps.

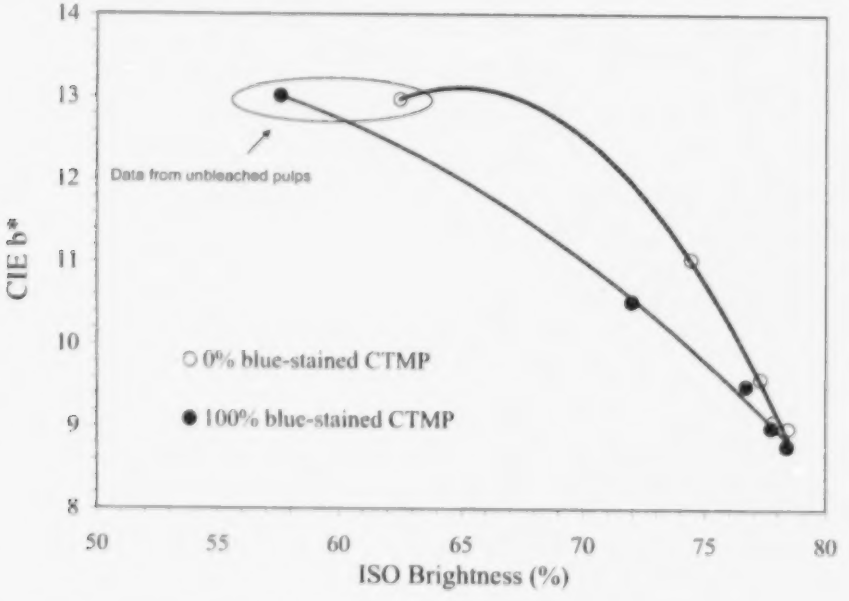

Figure 14. CIE b* vs. ISO brightness of the unbleached CTMP pulps and the pulps bleached with various amounts of alkaline hydrogen peroxide.

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